The University of Chicago

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A DISSERTATION SUBMITTED TO THE FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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GLEN R. SIMMONS

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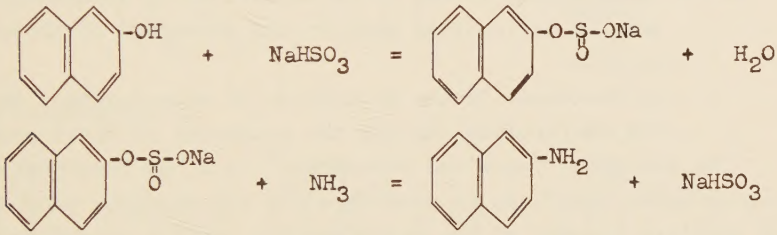
## INTRODUCTION

The simplest way to prepare an aromatic amine from the corresponding phenol is to treat the phenol with ammonia. This direct reaction does not proceed readily; fairly high temperatures and pressures as well as condensation agents are required to obtain satisfactory yields. The reaction is reversible; amines heated with water at sufficiently high temperatures are converted into phenols.

In 1899 and 1901 Bucherer[1] patented a process for the rapid amination of naphthols at low temperatures by the use of sulfite or bisulfite catalysts. The application and interpretation of this reaction were discussed from 1904 to 1910 in a series of articles[2] in which Bucherer postulated the formation of an intermediate product, the sulfurous acid ester of the naphthol.



This interpretation was soon discredited by the following facts:

(1) The striking reactivity of the intermediate products does not agree with the behaviour of the neutral naphthol esters of sulfurous acid, which have since been prepared by treating naphthols with thionyl chloride.[3]

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[1]Bucherer, Ger. Patent 117,471 (1899); ibid., 121,683 (1901).

[2]Bucherer, J. prakt. Chem., 69, 49 (1904); ibid., 70, 345 (1904); Bucherer and Stohman, ibid., 71, 433 (1905); Bucherer and Seyde, ibid., 75, 249 (1907); ibid., 77, 403 (1908); Bucherer and Schmidt, ibid., 79, 369 (1909); Bucherer and Uhlmann, ibid., 80, 201 (1910); Bucherer and Sonnenberg, ibid., 81, 1 (1910).

[3]Richter, Ber., 49, 2339 (1916).

(2) Esterification is catalyzed by the hydrogen ion, and consequently, takes place more readily with strong acids than with weak. However, Franzen and Kempf,[4] in a study of the hydrolytic effect of various acids on aromatic amines, found that only sulfurous and hypo-phosphorous acids had an appreciable effect.

(3) The composition of the intermediate products, as determined by Vorozhtzov[5] in the cases of 1,5-diamino-naphthalene, 1,8-amino-naphthol, and the 4-, 5-, and 8-sulfonic acids of alpha-naphthol, indicates the addition of one mole of bisulfite to one mole of naphthol without loss of water.

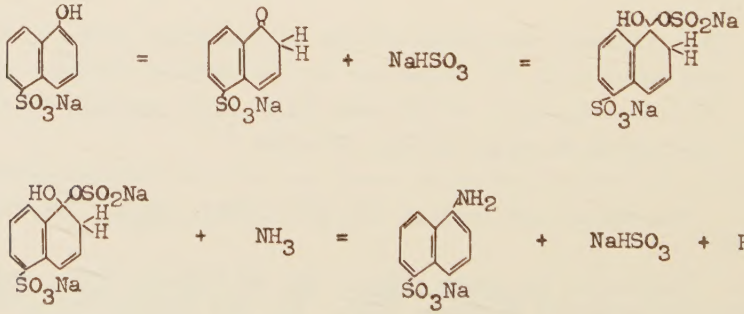
(4) Many exceptional instances of bisulfite-catalyzed amination are not explained by the ester-intermediate product theory.

(a) Phenol and its derivatives are not readily converted by ammonia into amines, even in the presence of sulfites or bisulfites.

(b) Substituents in the 2- or 3-position of alpha-naphthol and its derivatives inhibit the amination of these phenols.

(c) Substituents in the 4-position of beta-naphthol and its derivatives inhibit the amination of these phenols.

The preceding facts led Vorozhtzov[6] to a new interpretation of the Bucherer reaction; he considers the intermediate product to be an addition product of the bisulfite ion and the keto-form of the naphthol.

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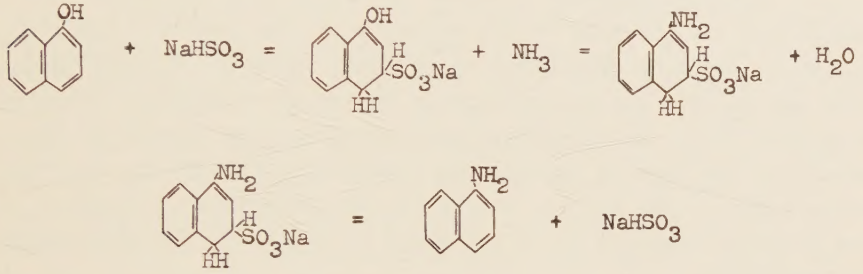
[4] Franzen and Kempf, Ber., 50, 101 (1917).

[5] Vorozhtzov, Ann. de Chim. (9), 7, 50 (1917).

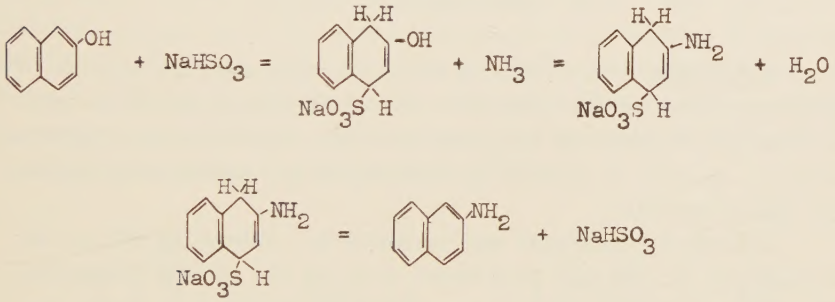
[6] Ibid., 6, 381 (1916).

This theory agrees with the composition of the intermediate product as determined by analysis. It is free from most of the objections to the esterification hypothesis, but it offers no explanation of the various exceptional reactions. Moreover, Vorozhtzov's formula is that of a carbonyl-bisulfite addition compound, whereas Raschig,[7] by his work on formaldehyde, has shown this type of compound to be a hydroxy-sulfonate.

In an attempt to meet the objections to Vorozhtzov's mechanism, Bogdavov[8] offered the following theory of the reaction. With alpha-naphthol:



With beta-naphthol:



This scheme explains the inhibiting effect of substituents in the 3-position in alpha-naphthol or in the 4-position in beta-naphthol, since the mechanism involves addition to the double bond in these positions. The theory is also supported by the analogy to 1,4-

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[7]Raschig, Ber., 59B, 859 (1926); Raschig and Prahl, ibid., 2025; ibid., 61B, 179 (1928); cf. Lauer and Langkammerer, J. Am. Chem. Soc., 57, 2360 (1935).

[8]Bogdanov, J. Gen. Chem., U.S.S.R., 2, 9 (1932).

addition reactions of alpha, beta unsaturated aldehydes and ketones, such as the addition of sodium bisulfite to cinnamaldehyde and to benzal acetophenone. Moreover, the carbon to sulfur linkage in sulfonic acids formed by the addition of bisulfites to ethylenic double bonds is resistant to hydrolysis by alkalies, whereas the carbon to sulfur linkage in keto-bisulfite addition compounds is easily broken by alkalies. Thus support for Bogdanov's mechanism is found in the resistance of certain phenol-bisulfite addition compounds (e.g., 1,5-dihydroxy-naphthalene-sodium bisulfite) to alkaline hydrolysis.

Although Bogdanov's scheme is better than any previously suggested, the question of the mechanism of the Bucherer reaction can by no means be considered as decided. Bogdanov's hypothesis does not explain the non-resistance of certain bisulfite addition compounds (e.g., 2,7-dihydroxy-naphthalene-sodium bisulfite) to alkalies, nor does it explain the hindrance exercised by adjacent substituents. The author, therefore, has undertaken a study of the Bucherer reaction in an endeavour to throw further light upon its mechanism.

## EXPERIMENTAL

Materials.--Chemicals used in the experimental work included anhydrous sodium bisulfite and monohydrated ammonium sulfite (Baker), resublimed beta-naphthol and alpha-nephthol (General Chemical), as well as sodium hypophosphite and ammonium hypophosphite (Mallinckrodt).

1-Methyl-2-naphthol was prepared by condensing 100 g. of beta-naphthol in 120 ml. of alcohol with 55 ml. of 40% formaldehyde. Sodium acetate (20 g.) was added as catalyst.[9] After the mixture had stood four days at room temperature, dinaphthylol methane was obtained from it in about theoretical yield. Dinaphthylol methane (100 g.) in a liter of water was heated for eight hours under reflux with 100 g. of sodium hydroxide and 125 g. of zinc dust. The preceding cycle of condensation and reduction was repeated three times for more complete conversion. The resulting

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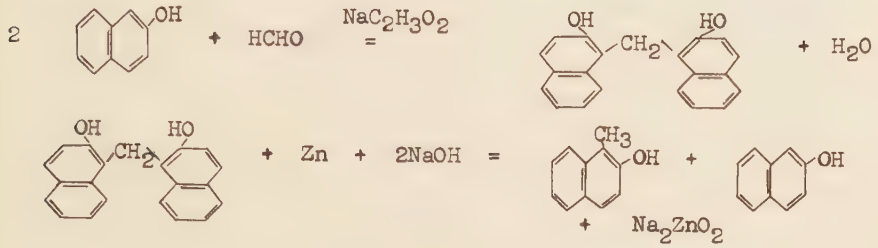
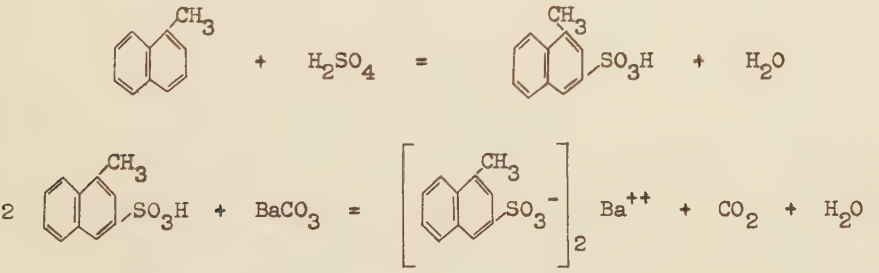
[9]Fries and Huebner, Ber., 39, 435 (1906).

product, crystallized repeatedly from large volumes of water, melted at 112°C.



4-Methyl-2-naphthol was prepared by the method of Vesely and Stursa.[10] 1-Methyl-naphthalene (100 g.) and 75 g. of concentrated sulfuric acid (d. 1.84) were heated with agitation for 5-6 hours at 110-120°C. After the mixture had cooled, it was dissolved in water, the hot solution neutralized with barium carbonate, and the precipitated barium sulfate removed by filtration. The barium salt of the sulfonic acid which crystallized from the cooled filtrate was recrystallized twice from water. Sodium carbonate was added to a solution of the first fraction in water. Barium carbonate was removed by filtration; the filtrate, reduced to a small volume, yielded 50 g. of sodium salt. This salt, dried and then ground with ten times its weight of potassium hydroxide, was heated first to 260°, and then to 280°C. The fused mass was dissolved in water and acidified with hydrochloric acid. 4-Methyl-2-naphthol precipitated, and was isolated by steam distillation as colorless needles, melting at 81-82°C.



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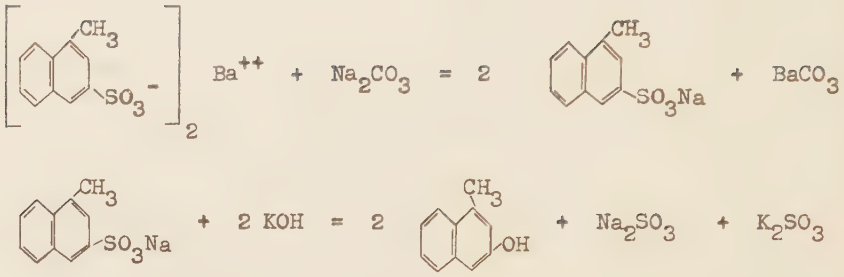
[10] Vesely and Stursa, Coll. Czech. Chem. Comm., 3, 328 (1931).



General method.--Reaction mixtures of naphthols, aqueous ammonia, and additional reagents, such as ammonium sulfite, ammonium hypophosphite, etc., were heated with agitation in a special oil bath in sealed glass tubes at various temperatures for various lengths of time. In some instances, additional solvents, such as alcohol, glycerol, etc., were used.

Preliminary work showed that practically no amine could be obtained by heating reaction mixtures of naphthols and aqueous ammonia in sealed glass tubes in an oil bath. (See Table 1A.) Since fairly satisfactory yields of amine were obtained by introducing solvents (alcohol or butyl cellosolve) or emulsifying agents (soap) (see Table 1A), it was decided that the difficulty with the pure reaction mixtures lay in their heterogeneity, even at high temperatures. A special oil bath in which these mixtures could be vigorously agitated was therefore built.

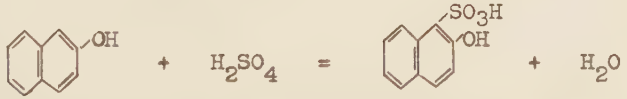
The apparatus consists of a tank, 14 in. by 14 in. by 5 1/2 in., welded from 16-gauge sheet steel and mounted on two steel rods ten inches above a base plate. The sealed tubes are held in four ten-inch and four nine-inch single extra-heavy pipes, threaded on the inside to take 3/4 in. plugs; these pipes are mounted, together with a large bicycle sprocket, on a plate centered on a shaft. Mounted above the oil bath on a second shaft is a small bicycle sprocket, connected to the larger sprocket by a chain. This second shaft carries a small pulley connected by a V-belt to a pulley on the slow speed shaft of a 33:1 speed reducing gear which is mounted on the base plate; the high speed shaft is directly coupled to the shaft of a 3500 rpm motor. In operation, the sealed tubes held in the pipes are turned end over end twenty-six times per minute, the highest speed found possible

without excessive spattering of the oil. Heating is accomplished principally by means of gas burners applied directly to the bottom of the tank, but additional heat and automatic temperature control is provided by a 250-watt knife-heater, controlled by a De Khotinsky thermo-regulator. This heating arrangement gives a uniform temperature ($\pm$ 0.3° at 153°C.) without the use of large amounts of electricity.

The reaction mixtures were analyzed by two methods; satisfactory checks were thus obtained.

(1) Isolation method.--The crude reaction mixture was filtered, and the residue, a mixture of naphthol, naphthylamine, etc. was extracted first with alkali to remove the unchanged naphthol, and then with acid to dissolve the naphthylamine. The dissolved naphthylamine was reprecipitated with alkali, filtered, dried, and weighed. Melting points were taken to check purity, and recrystallizations were made whenever necessary. Recovery of unchanged naphthol was used as a check on the efficiency of the method.

(2) Titration method.[11]--Since primary amines can be quantitatively determined by titration with nitrous acid, a quantitative analytical method of this type can be used for beta-naphthylamine in the presence of beta-naphthol. The alpha-position of both compounds must be blocked by a substituent to prevent the formation of alpha-nitroso compounds. Those derivatives of beta-naphthol which do not have substituents in the alpha-position may have this position blocked by sulfonation at low temperatures.




The procedure of the titration method was as follows: The reaction mixture was evaporated to dryness, and then treated with concentrated sulfuric acid at 0-5°C. The temperature was allowed to rise to 40°C., and the mixture was then poured on ice. The resulting solution was boiled to expel sulfur dioxide, cooled, and diluted to a standard

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[11] Lee and Jones, J. Ind. Eng. Chem., 14, 961 (1922).

volume; aliquot portions were titrated with standard sodium nitrite solution, starch-iodide being used as an external indicator.

Preliminary work.--Before the employment of the special oil bath, work done on the catalyzed conversion of alpha- and beta-naphthols to the corresponding naphthylamines showed that:

(1) The use of solvents and emulsifying agents improves the yield of amines from naphthols. (See Table 1A.)

(2) The best yields of amines are obtained at temperatures of 150-160°C. At lower temperatures the yield is decreased by the slowness of the reaction; at higher temperatures beta-beta-dinaphthylamine is formed. (See Table 1B.)

(3) Increase in concentration of ammonia increases yield. (See Table 1C.)

(4) Lengthening of the time of heating increases the yield up to the point where the yield is lowered by the formation of beta-beta-dinaphthylamine. (See Table 1D.)

TABLE 1

PRELIMINARY WORK

| Reaction Mixture | Conditions of Reaction | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|
| | Time Hours | Temp. °C. | | |
| **A. Effect of Solvents on Yield of Amine** | | | | |
| 10.00 g. beta-naphthol<br>10 ml. 20% ammonia<br>15 ml. 40% ammonium sulfite | 5<br>7 1/2<br>12 | 155<br>155<br>155 | | 0<br>1<br>3 |
| 5,000 g. beta-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. ethyl alcohol | 20<br>28<br>12 1/2 | 155<br>165<br>155 | <br><br>1<br>2 | 50<br>60<br>63<br>64 |
| 5.000 g. beta-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. butyl cellosolve | 25 | 155 | | 60 |
| 5.000 g. beta-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>1 ml. oleic acid | 25 | 155 | | 62 |

TABLE 1--Continued

| Reaction Mixture | Conditions of Reaction | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|
| | Time Hours | Temp. °C. | | |
| **B. Effect of Temperature on Yield of Amine** | | | | |
| 5.000 g. beta-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. ethyl alcohol | 20<br>20<br>20 | 100<br>155<br>200 | | 1<br>50<br>30 |
| 5.000 g. beta-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. butyl cellosolve | 25<br>25<br><br>25 | 100<br>155<br><br>200 | <br>1<br>2 | 1<br>60<br>64<br>1 |
| 5.000 g. alpha-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. butyl cellosolve | 25<br>25 | 100<br>200 | | 1<br>0 |
| 5.000 g. alpha-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>1 ml. oleic acid | 25 | 155 | | 64 |
| **C. Effect of Concentration of Ammonia on Yield of Amine** | | | | |
| 5.000 g. beta-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. ethyl alcohol | 25 | 155 | | 50 |
| 5.000 g. beta-naphthol<br>15 ml. 28% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. ethyl alcohol | 25 | 155 | | 84 |
| **D. Effect of Length of Time of Heating on Yield of Amine** | | | | |
| 5.000 g. beta-naphthol<br>10 ml. 20% ammonia<br>7.5 ml. 40% ammonium sulfite<br>10 ml. ethyl alcohol | 4<br><br>8<br><br>12 1/2<br><br>43<br><br>75 | 155<br><br>155<br><br>155<br><br>155<br><br>155 | 1<br>2<br><br>1<br>2<br><br>1<br>2<br><br> | 41<br>38<br><br>40<br>35<br><br>63<br>64<br><br>74<br><br>70 |

Results obtained with agitated reaction mixtures.--The preliminary work led to the adoption of the following standardized procedure in most of the runs with the special oil bath:

(1) The weight of naphthol used was 2.000 g.
(2) The volume of 20% ammonia solution was kept constant at 4.0 ml.
(3) The volume of 40% ammonium sulfite solution was kept constant at 4.0 ml.
(4) The temperature was maintained at 153°C. for 12 hours.
(5) When additional solvents were used, the volume selected was usually 4.0 ml.
(6) When additional reagents were used, the weight taken was 2.000 g.
(7) In testing substances other than ammonium sulfite for catalytic activity, the amount equivalent to 4.0 ml. of 40% ammonium sulfite was employed.

Determination of catalytic activity of ammonium sulfite (see Table 2).--Yields of approximately 90% of primary amine are obtained from beta-naphthol in 12 hours at 153°C. with ammonia and ammonium sulfite, whereas less than 10% are obtained with ammonia alone. Alpha-naphthol and ammonia without a catalyst give only a trace of amine, but, when ammonium sulfite is used, the yields are satisfactory.

Effect of ammonium chloride (see Table 2).--Ammonium chloride in the reaction mixture increases the yield of amine (21.7% average with water as a solvent and 27.0% average with glycerol added), but yields still remain much lower than those obtained when sulfite is present. This fact indicates that there is a special effect of the sulfite ion beyond the common ion effect of the ammonium salt.

Determination of the effect of oxygen (see Table 4).--The catalytic activity of sulfite does not depend upon the presence of oxygen. There is no difference between the yield obtained from an ordinary reaction mixture and that obtained from a mixture completely freed of oxygen by repeated evacuation of the tube to very low pressures (less than $10^{-5}$ mm. of mercury) before sealing.

Catalytic effects of substances other than sulfites (see Table 5).--An attempt was made to elucidate the catalytic action of ammonium sulfite by studying the catalytic effects of compounds

TABLE 2

DETERMINATION OF CATALYTIC ACTIVITY OF AMMONIUM SULFITE

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia | 12 | 153 | Agitated | 1<br>2<br>3<br>4 | 9.8<br>9.1<br>9.1<br>8.1 |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>4.0 ml. 40% ammonium sulfite | 12 | 153 | Agitated | 1<br>2<br>3<br>4 | 87.0<br>90.6<br>92.5<br>91.2 |
| 2.000 g. alpha-naphthol<br>4.0 ml. 20% ammonia<br>4.0 ml. water | 12 | 153 | Agitated | 1<br>2 | Trace<br>Trace |
| 2.000 g. alpha-naphthol<br>4.0 ml. 20% ammonia<br>4.0 ml. 40% ammonium sulfite | 12 | 153 | Agitated | 1<br>2 | 55.9<br>73.0 |

with analogous electronic structures. Since there are two possible structures of the bisulfite ion, namely, the hydrosulfonate ($H\text{-}SO_2O^-$), and the normal bisulfite ($^{O=S-OH}_{\ O^-}$), two kinds of substances were chosen, those such as hypophosphite ($^{H_2P=O}_{\ O^-}$), similar in structure to the hydrosulfonate, and those such as biselenite ($^{O=Se-OH}_{\ O^-}$), analogous to the normal bisulfite.

(1) Ammonium selenite.--Ammonium selenite was substituted for ammonium sulfite in the reaction mixture of a standard run, but no amine was obtained. The presence of elementary selenium in the mixture after heating indicated that oxidation had occurred.

(2) Ammonium arsenite.--Ammonium arsenite gives slightly poorer yields of amine than does ammonium chloride. It cannot therefore be considered as a true catalyst, for the slight increase in yield is due only to the common ion effect. When arsenious oxide dissolved in sodium hydroxide rather than in ammonium hydroxide is used, the yield is decreased.

TABLE 3

EFFECT OF AMMONIUM CHLORIDE

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>4.0 ml. 40% ammonium sulfite<br>2.000 g. ammonium chloride | 12 | 153 | Agitated | 1<br>2 | 89.2<br>70.5 |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>2.000 g. ammonium chloride<br>3.6 ml. water | 12 | 153 | Agitated | 1<br>2 | 20.4<br>22.8 |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>5.0 g. glycerol<br>2.000 g. ammonium chloride | 12 | 153 | Agitated | 1<br>2 | 26.0<br>28.0 |

TABLE 4

DETERMINATION OF THE EFFECT OF OXYGEN

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>4.0 ml. 40% ammonium sulfite | 12 | 153 | Agitated<br>Evacuated | 1<br>2 | 90.5<br>90.6 |

(3) Ammonium antimonite.--Ammonium antimonite is also not a true catalyst, since it yields no greater amount of amine than is obtained with ammonium chloride.

(4) Sodium hypophosphite.--Sodium hypophosphite gives slightly better yields than does ammonia alone; it may therefore be considered to show a small catalytic effect. This effect

is, however, not comparable with the marked effect exercised by sulfite ion.

(5) Ammonium dihydrogen phosphite.--The results obtained with ammonium dihydrogen phosphite are analogous to those obtained with ammonium chloride; no true catalytic effect was observed.

Determination of effect on yield of length of time of heating (see Table 6).--Standard reaction mixtures were heated for various lengths of time. The yield of amine improved up to twelve hours heating, when a maximum of 92.5% was reached. Longer periods of heating lowered the yield of amine; condensation products were isolated from the reaction mixtures thus treated.

TABLE 5

CATALYTIC EFFECTS OF SUBSTANCES OTHER THAN SULFITES

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. beta-naphthol<br>5.4 ml. 20% ammonia<br>1.600 g. selenium dioxide<br>3.6 ml. water | 12 | 153 | Agitated | 1<br>2 | 0<br>0 |
| 2.000 g. beta-naphthol<br>5.4 ml. 20% ammonia<br>1.400 g. arsenious oxide | 12 | 153 | Agitated | 1<br>2 | 15.8<br>15.7 |
| 2.000 g. beta-naphthol<br>5.4 ml. 20% ammonia<br>1.400 g. arsenious oxide<br>0.5656 g. sodium hydroxide<br>3.5 ml. water | 12 | 153 | Agitated | 1<br>2 | 4.1<br>2.6 |
| 2.000 g. beta-naphthol<br>5.4 ml. 20% ammonia<br>2.050 g. antimonous oxide<br>3.6 ml. water | 12 | 153 | Agitated | 1<br>2 | 8.3<br>13.6 |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>1.505 g. $NaH_2PO_2.H_2O$<br>2.5 ml. water | 12 | 153 | Agitated | 1<br>2 | 13.6<br>12.2 |
| 2.000 g. beta-naphthol<br>4.0 ml. 25% ammonia<br>3.7 ml. 40% $NH_4H_2PO_3$ | 12 | 153 | Agitated | 1<br>2 | 17.8<br>17.5 |

TABLE 6

EFFECT OF LENGTH OF TIME OF HEATING ON YIELD OF AMINE

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>4.0 ml. 40% ammonium sulfite | 2 | 153 | Agitated | 1<br>2<br>3 | 12.2<br>11.8<br>9.7 |
| | 3.5 | 153 | Agitated | 1<br>2 | 30.9<br>28.6 |
| | 8 | 153 | Agitated | | 83.3 |
| | 10 | 153 | Agitated | 1<br>2 | 86.1<br>88.0 |
| | 12 | 153 | Agitated | 1<br>2<br>3<br>4 | 92.5<br>91.2<br>87.0<br>90.6 |
| | 20 | 153 | Agitated | | 88.2 |
| | 25 | 153 | Agitated | | 86.5 |

Substituted naphthols in the Bucherer reaction (see Table 7).--In order to determine the effects of introduction of substituents in the naphthalene ring, 1-methyl-2-naphthol and 4-methyl-2-naphthol were prepared and treated under similar conditions to those used with beta-naphthol.

(1) 1-Methyl-2-naphthol.--1-Methyl-2-naphthol, when treated according to the standard procedure, gives very low yields of amine. Only 11% was obtained when the reaction time was doubled; even with longer periods of heating, with or without added ammonium sulfite, the yields of amine were always low. A substituent in the 1-position of beta-naphthol evidently inhibits both the amination itself and the catalysis of the amination.

(2) 4-Methyl-2-naphthol.--No amine could be isolated after treatment of 4-methyl-2-naphthol according to the standard procedure. A substituent in the 4-position of beta-naphthol

completely inhibits the reaction under the conditions of the experiment.

Substitution of dimethylamine for ammonia (see Table 8).--Dimethylamine was found to react with beta-naphthol much better than does ammonia. More than twice as much amine was obtained under comparable conditions. When sodium hydrogen sulfite was used as a catalyst, high yields were obtained.

TABLE 7

SUBSTITUTED NAPHTHOLS IN THE BUCHERER REACTION

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. 1-methyl-2-naphthol<br>3.65 ml. 20% ammonia<br>3.65 ml. 40% ammonium sulfite | 12 | 153 | Agitated | 1<br>2 | Trace<br>Trace |
| | 24 | 153 | Agitated | 1<br>2 | 11.7<br>11.1 |
| | 80 | 153 | Agitated | 1<br>2 | 10.3<br>14.0 |
| 2.000 g. 1-methyl-2-naphthol<br>3.65 ml. 20% ammonia<br>3.65 ml. water | 80 | 153 | Agitated | 1<br>2 | 9.0<br>6.5 |
| 2.000 g. 4-methyl-2-naphthol<br>3.65 ml. 20% ammonia<br>3.65 ml. 40% ammonium sulfite | 12 | 153 | Agitated | 1<br>2 | 0<br>0 |

TABLE 8

SUBSTITUTION OF DIMETHYLAMINE FOR AMMONIA

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. beta-naphthol<br>4.0 ml. 33% dimethylamine<br>2.000 g. sodium bisulfite | 12 | 153 | Agitated | 1<br>2 | 88.0<br>88.0 |

Solvent effects of alcohol and glycerol (see Table 9).-- In an effort to obtain a one-phase reaction mixture, alcohol and glycerol were tried as solvents. Standard mixtures with alcohol replacing part of the water as solvent gave much lower yields (34-36%) than did water alone. Glycerol proved to be a better solvent; yields of amine as high as 80% were obtained. However, since glycerol cannot readily be separated by evaporation from the reaction products, yield determination of amine by the isolation method is difficult when glycerol is present.

TABLE 9

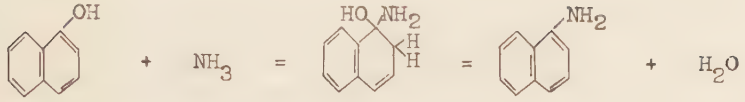
SOLVENT EFFECTS OF ALCOHOL AND GLYCEROL

| Reaction Mixture | Conditions of Reaction | | | Number of Run | Yield of Primary Amine % |
|---|---|---|---|---|---|
| | Time Hrs. | Temp. °C. | Other | | |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>1.90 g. $(NH_4)_2SO_3.H_2O$<br>4.0 ml. alcohol | 12 | 153 | Agitated | 1<br>2 | 11.1<br>11.9 |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>4.0 ml. 40% ammonium sulfite<br>4.0 ml. alcohol | 12 | 153 | Agitated | 1<br>2 | 36.5<br>34.6 |
| 2.000 g. beta-naphthol<br>4.0 ml. 20% ammonia<br>1.9 g. $(NH_4)_2SO_3.H_2O$<br>5.0 ml. glycerol | 12 | 153 | Agitated | 1<br>2 | 81.9<br>83.4 |

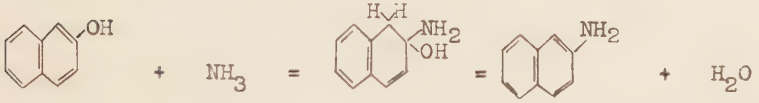
## DISCUSSION

Little attention has been paid in the literature to the basic reaction in the amination of naphthols, namely, the action of ammonia without a catalyst. This reaction proceeds slowly; heating at 153°C. for twelve hours gives a yield of about 9%. The mechanism is probably addition of ammonia to the 1,2-double bond of the naphthol followed by loss of water. The reverse reaction would then be addition of water to the 1,2-double bond of the naphthylamine with subsequent loss of ammonia.

In the case of alpha-naphthol:



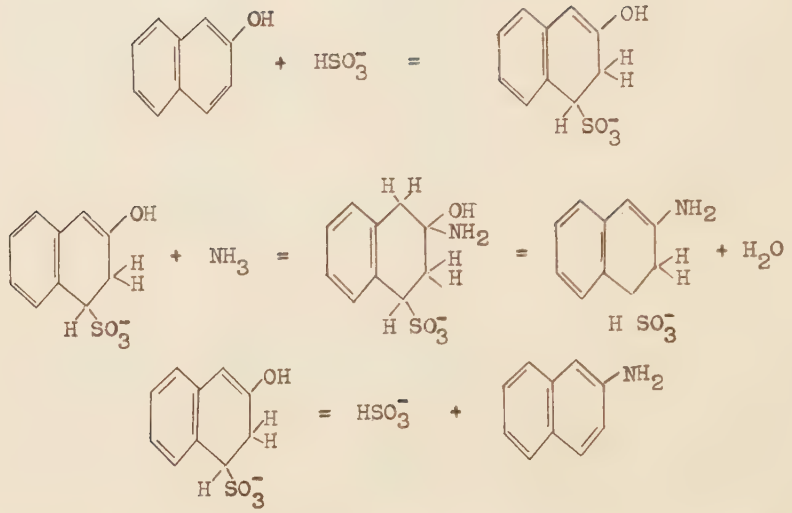
In the case of beta-naphthol:



This explanation is substantiated by the fact that substitution in the 1-position in beta-naphthol greatly inhibits the reaction. For example, even in the presence of a catalyst, the degree of conversion of 1-methyl-2-naphthol into amine is much less than the conversion, under similar conditions, in the case of the uncatalyzed reaction between beta-naphthol and ammonia.

The question then arises as to the nature of the sulfite catalysis. Does the addition of ammonia to the 1,2-double bond take place in the manner indicated in the preceding discussion, but facilitated by the preliminary addition of bisulfite to the naphthalene ring, or does the reaction proceed in some entirely different way? Considering the latter assumption, it may be noted that some support is afforded Vorozhtzov's hypothesis in that the yield of 1-methyl-2-naphthylamine from 1-methyl-2-naphthol is not increased to any appreciable extent by the presence of the bisulfite catalyst; this would suggest the mechanism of addition of the bisulfite to the 1,2-position. However, an unproved complication is introduced in this mechanism in the requirement that the intermediate product formed react with ammonia in a manner different from that postulated for the reaction of naphthol itself with ammonia.

According to the former supposition, the bisulfite must add in such a way that the 1,2-double bond is not destroyed; that is to say, in the case of beta-naphthol, the bisulfite must add either in the 3,4- or in the 1,4-position. In the latter case the primary addition product must rearrange to give the 3,4-addition product.



The greater reactivity of this addition product can be explained by the fact that it is a dihydro-naphthalene derivative, and, as such, would more readily add ammonia to the remaining double bond.

If the preceding assumption be correct, substitution in the 4-position in beta-naphthol should inhibit the catalysis of the amination, but should not completely prevent the amination itself. Under ordinary conditions 4-methyl-2-naphthol was found to give no amine even with catalyst. Vesely and Stursa,[12] however, have reported the preparation of some amine from 4-methyl-2-naphthol under extreme conditions (240°C. in an autoclave). This would indicate an inhibition of catalytic action without absolute prevention of amination.

In the mechanism offered here, the bisulfite is assumed to add in the same manner as it adds to ethylenic double bonds, namely, as the hydrosulfonate. This is supported by the fact that hypophosphite also acts as a catalyst in the amination of naphthols; its structure is analogous to that of the hydrosulfonate.

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[12] Vesely and Stursa, op. cit.

## SUMMARY

1. It was shown that ammonium sulfite increases tenfold the yield of primary amine from beta-naphthol by amination with ammonia, whereas other ammonium salts approximately double the yield.
2. The catalytic activity of sulfites was shown to be independent of the presence of oxygen.
3. A search for other substances with catalytic activity in amination of naphthols revealed that only hypophosphites have a measurable effect; sodium hypophosphite increases the yield by about 40%.
4. Substitution of the 1-position in beta-naphthol was found to eliminate the catalytic action of sulfites and also to decrease greatly the amination by ammonia without catalyst.
5. The substitution of the 4-position in beta-naphthol was found to prevent amination completely in the presence of sulfites under moderate reaction conditions.
6. A study was made of the effects of time of heating, temperature, and presence of solvents on yield of amine from sulfite-catalyzed reactions of naphthols.